THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

BY

SISTER MARY MARTINETTE HAGAN, B.V.M.

B.A., Clarke College, 1933
M.S., Saint Louis University, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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ACKNOWLEDGMENT

It is a pleasure to acknowledge the interest and guidance of Professor John C. Bailar, Jr., who both instigated and directed this research. The writer is also deeply indebted to the Congregation of the Sisters of Charity of the Blessed Virgin Mary of which she is a member. Through their generosity both time and financial aid were made available to her for this study.

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THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

The effect of steric hindrance upon the tendencies of certain groups to substitute within the coordination sphere of a complex inorganic molecule was first noted by Jaeger. He observed the phenomenon while working with *tris*-ethylenediamine complexes of cobalt and rhodium (1). Assuming a certain number of isomerides to be possible, and each one of them to have its own spatial arrangement, he postulated a degree of resistance on the part of the molecule to the admission of certain groups to the disymmetrical coordination sphere. He believed this resistance to be due to steric hindrance.

Bailar (2) and co-workers have carried out a series of investigations which appear to confirm Jaeger's postulate concerning the selective directing influence of the complex ion upon the group entering its coordination sphere. They have proposed the application of this phenomenon to the resolution of racemic mixtures. Tartaric acid may readily be introduced into the coordination sphere of certain cobalt complexes. According to Bailar's proposal either *dextro*-tartrate ion or *levo*-tartrate ion should coordinate with greater facility.

In order to test the applicability of this proposal several experiments were carried out. In the preparation of materials for the resolution studies on *racemic*-tartaric acid an interesting observation was made concerning the optical activity of [Co *l*-pn_2CO_3]Cl. A number of 0.1% solutions of the complex were prepared and found to be optically unstable at 10° C., at room temperature and at elevated temperatures. When a solution of the complex was evaporated to dryness at room temperature the specific rotation of a 0.1% solution of the complex formed was +130°. When it was evaporated to dryness on a steam cone at 80-85° C. the specific rotation of a 0.1% solution of the compound formed was −410°. Both solutions on standing at room temperature underwent a change in rotation and in

each case the change was an increase in the positive direction. These data seemed to indicate the preparation of the diastereoisomers, [Co *l*-pn_2CO_3]Cl and [Co *l*-pn_2CO_3]Cl (3).
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Absorption curves were determined for these two carbonato solutions. The shape of the two curves was very similar but the light absorption for the *dextro*-rotatory isomer was lower at all wave lengths than for the *levo*-rotatory isomer. Rotatory dispersion curves were determined for each solution and were found to differ markedly. Super-imposition of the absorption curves on the rotatory dispersion curves shows the rotatory power to increase strongly as one approaches the region of maximum absorption and to change sign within this region. These results are those predicted for colored complex molecules and are examples of the Cotton Effect (4).

Similarly, in the preparation of the *dextro*- and *levo*-tartrato complexes of *bis-levo*-propylenediamine cobalt chloride the isomers were found to have specific rotations of — 80° and + 70° respectively, at the D line of sodium. The complex mixture which was prepared using *racemic*-tartaric acid, i.e. [Co *l*-pn_2*d*-tart]Cl and [Co *l*-pn_2*l*-tart]Cl, was optically inactive at the D line of sodium. Optically the *dextro*-tartrato complex was more stable than the *levo*-tartrato complex; however, 0.1% solutions of both changed rotation on heating at 85-90° C. A 0.1% solution of the complex mixture made from *racemic*-tartaric acid became *dextro*-rotatory on heating while the rotation of a 0.1% solution of *levo*-tartrato complex became more positive and the rotation of a 0.1% solution of the *dextro*-tartrato complex became more negative on heating under the same conditions. Both the *levo*-tartrato and the *dextro*-tartrato solutions undoubtedly contained mixtures of their respective diastereoisomers.

The proposal of preferred coordination implies a difference in the chemical stabilities of the complex ions. The rate at which the two tartrato complexes are converted to the dinitro-*bis-levo*-propylenediamine complex was studied by measure-

ments of the absorption of light, the absorption peaks of the tartrato and the dinitro complexes being at quite different wave lengths. The rate of decrease in the heights of the tartrato peaks and the rate of increase in the height of the dinitro peak were used to calculate the respective concentrations at the reaction times chosen. These measurements showed the *levo*-tartrato complex to react more rapidly than the *dextro*-tartrato complex. It was also apparent from them that there was an optimum time at which the difference in the reaction rates was most marked. From the extinction coefficients calculated for the *dextro*- and the *levo*-tartrato complex mixtures after the reaction had proceeded for two hours and fifteen minutes the approximate amounts of the complexes which had reacted was calculated. These data showed 11% of the *dextro*-tartrato complex to have reacted and 47% of the *levo*-tartrato complex to have reacted. From the curve this appeared to be the point at which the greatest difference was to be found.

A study of the rate of conversion of the tartrato complexes to *tris-levo*-propylenediamine cobalt (III) chloride was unsuccessful. Evidently the reaction is not a simple conversion of one complex to the other.

The resolution of *racemic*-tartaric acid was attempted by treating the complex mixture made from *racemic*-tartaric acid, [Co *l*-pn_2*d*-tart]Cl + [Co *l*-pn_2*l*-tart]Cl, with *racemic*-tartaric acid. The reaction was carried out at 85-90° C. for sixteen hours and on evaporating the solution to dryness separation of the tartaric acid from the cobalt complex was effected by dissolving the mixture in water and passing the solution through an amberlite resin Ion Exchange column (5). The tartaric acid obtained was optically inactive. Under the conditions employed here, resolution by this means does not appear to be feasible.

A critical study of this reaction seemed to indicate the use of *dextro*-tartaric acid, rather than *racemic*-tartaric acid. Since the investigations of Jonassen (6) and of Hamilton (7)

showed the *dextro*-tartrate ion to coordinate in preference to the *levo*-tartrate ion, the reaction of [Co *l*-pn_2*d*-tart]Cl + [Co *l*-pn_2*l*-tart]Cl with *dextro*-tartaric acid was carried out at 85-90° C. for forty-eight hours, using a 2:1 molar ratio of complex compound to acid. The resulting free acid was separated from the mixture by Ion Exchange methods and, on the basis of calculations from the specific rotation measurements, 46.3% of the *levo*-tartaric acid was found to have been released from the coordination sphere. Changing the molar ratio of the complex compound to acid from 2:1 to 1:1 and repeating the experiment produced free tartaric acid in which 69.3% of the *levo*-tartaric acid was found to have been released from the coordination sphere. There is always the possibility of random distribution between complexed and uncomplexed tartarate as the cause of this apparent partial resolution; however, the amount of *levo*-tartaric acid released was always greater than that attributable to random distribution alone.

These resolution experiments using *dextro*-tartaric acid give good evidence in favor of the proposal of preferred coordination as a means of bringing about the resolution of *racemic*-tartaric acid. The procedure has no practical value because of the presence of excess *dextro*-tartaric acid which prevents the isolation of free *levo*-tartaric acid. By changing concentrations, temperatures and reaction times, and with the addition of a suitable catalyst, it is possible that the yield of *levo*-tartaric acid may be increased.

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